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(54) An improved method for dyeing and printing of polyolefins

(57) The invention concerns an improved method for dyeing or printing of polyolefin, preferably polyolefin which have been modified by melt blending 100 parts per weight of polyolefin with 1-20 parts per weight of copolymer of ethylene and dialkylaminoalkyl methacrylamide of methacrylate and with 0-3 part per weight of alkali metal salt of organic carboxylic acid, or for dyeing or printing fibers or fiber products made from the polyolefin, in which method the dye bath comprises a dyeing auxiliary which is of the general formula (I)

$$R - O -((CH_2)_n - O)_m CH_2 - COOH \qquad (I)$$

where

- R is a fatty alcohol radical having from 8 to 24 carbon atoms or an alkylphenol where the alkyl part contains from 8 to 9 carbon atoms
- n is 2 or 3
- m is from 0 to 150.

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Description

This invention relates to an improved method for dyeing and printing of polyolefins. Especially the invention relates in improvements of fixation speed of acid dyes on acid dyeable polyolefins. Also, the invention relates to fibers and articles made of these fibres containing this dyeable polyolefin.

Polyolefins such as polypropylene and polyethylene have excellent physical and mechanical properties and excellent processability. However, the dyeing of polyolefins, especially polypropylene, polyolefin fibers and articles made from the fibers with conventional acid dyes and dyeing technologies has been very difficult because of the hydrophobicity and the lack of sites where hydrogen bonds or electrostatic attraction can operate, it has been very difficult to dye fabricated articles of these polymers. In particular, crystalline polypropylene fibers are lightweight and strong and they have good heat-retaining properties. These fibers have been expected to have wide applications, but have still limited use because it has not been able to dye them by ordinary dyeing methods.

Some improvements in dyeing of polypropylene has been achieved by some methods given in the patent literature. In EP 39207 there is given a dyeable polyolefin, which is obtained by blending 0,1 - 30 % by weight ethylene/aminoalkylacrylatecopolymer. Preferably it is a copolymer of ethylene and dimethylaminoethylmethacrylate.

Also EP 269293 describes a method to incorporate dyesites in polyolefin matrix in order to obtain electrostatic attraction between acid dyestuffs and the polyolefin matrix. In this publications the corresponding copolymer is a copolymer of ethylene and dialkyl aminoalkylacrylamide. This the dyeable composition comprises 100 parts per weight polyolefin, 1-20 parts per weight the above mentioned copolymer and also 0-3 parts per weight at least one alkali metal salt of an organic carboxylic acid having 7-24 carbon atoms.

The problem with the above mentioned compositions has, however, been that the dyeing speed is too slow to have commercial attractiveness in the today used dyeing machines, especially in printing, where the fixation speed of the dye is the most important dyeing criteria.

Although the above mentioned modified polyolefins, especially polypropylenes, contain functional groups rendering it dyeable with acid dyes, still the polypropylene matrix is very unpolar and therfor hydrophobic. A way to obtain deep enough colours with very long dyeing times is not attractive.

Acid dyes are polar and water soluble and the dyeing happens from an aqueous solution. The combination of polar and unpolar phases is the subject of this invention.

It has now surprisingly been invented that by adding some suitable auxiliaries in the exhaust dyebath, continuous dyeing liquor or printing paste the dyeing speed can be considerably improved. The principle is to have suitable products with optimal hydrophobic/hydrophilic balance acting as a compatibiliser between the unpolar substrate and the polar dyestuffs. By using the specific developed chemicals the fixation speed of dyes on the specifically modified polyolefin is greatly improved.

The auxiliaries according to this invention are fatty alcohols or alkyl phenols of polyalkoxylated carboxylic acids of general formula (I):

$$R - O - ((CH_2)_n - O)_m - CH_2 - COOH \qquad (I)$$

where

- R is a fatty alcohol radical having from 8 to 24 carbon atoms or an alkylphenol radical where the alkyl part contains from 8 to 9 carbon atoms
- n is 2 or 3
- m is from 0 to 150,

preferably in (I)

- R is a natural fatty alcohol radical based on coconut oil with 12 to 14 carbon atoms
- n is 2 or 3
- m is from 2.5 to 10

Typical addition levels of the auxiliary (I) are 2-50 g/kg for printing paste, from 0.1-5 % on weight of fabric (owf) for exhaust dyeing and 1-50 g/litre for continuous dyeing applications, in particular with a liquid Pick Up (P.U.) of 100 %.

The lower addition levels are for light shades, and the higher addition levels are for deep shades.

This invention further concerns the fibers made from the dyeable polyolefin composition and the articles made from these fibers.

The dyeable polyolefin composition according to this invention comprises a melt blended mixture of

- (A) 100 parts by weight of polyolefin
- (B) 1-20 parts by weight of an ethylene copolymer comprising 40 -95 % by weight ethylene and 5-60 % by weight at least one dialkylaminoalkyl methacrylamide or dialkylaminoalkyl methacrylate.
- (C) 0-3 parts by weight of at least one alkali metal salt of organic carboxylic acid having from 7 to 24 carbon atoms
- conventional additives, like stabilisers (antioxidants, UV stabilisers)

Preferably the polyolefin composition comprises

- (A) 100 parts by weight of polypropylene
- (B) 1-20 parts by weight, of an ethylene copolymer comprising 40 -95 % by weight ethylene and 5-60 % by weight dimethylaminopropyl methacrylamide (DMAPMA)

- (C) 0-3 parts by weight of at least one alkali metal salt of an organic carboxylic acid having from 7 to 24 carbon atoms
- conventional additives, like stabilisers (antioxidants, UV stabilisers)

The polyolefins (A) used in this invention are crystalline homopolymers of α-olefins like polyethylene, polypropylene, polybutene-1, poly-4-methylpentene-1 or various crystalline copolymers of those α-olefins. Most preferably the polyolefin is crystalline homopolymer or copolymer of propylene. The suitable melt index of polyolefins is 0.5 - 800.

Suitable dialkylaminoalkyl methacrylamide or methacrylate comonomers for ethylene copolymers (B) are for example dimethylaminoethyl methacrylamide or methacryate, dimethylaminopropyl methacrylamide or methacrylate diethylaminoethyl methacrylamide or methacrylate. Generally, the alkyl groups are C_1-C_4 alkyl groups, but most preferably the comonomer is dimethylaminopropyl methacrylamide.

A suitable proportion of the comonomer unit in the ethylene copolymer is 5-60 % by weight, preferably 10-50 % by weight.

In the modified polyolefin, the amount of ethylene copolymer (B) is 1-20 parts per weigth, based on 100 parts per weight polyolefin, preferably 2-10 parts per weight.

The alkali metal salt of an organic carboxylic acid (C) is e.g. sodium, potassium or lithium salt of organic acids, such as higher fatty acids having 10-24 carbon atoms, aromatic acids or nicotinic acids. Sodium or potassium stearate or benzoate, sodium p-tert-butylbenzoate or sodium nicotinate are preferred.

The composition can be produced by conventional mixing methods, preferably by melt blending using an extruder or other suitable equipment.

The dyeable polyolefin composition can be formed into fibers by conventional methods like melt spinning methods, but can also be fabricated into other forms such as films, sheets, tubes and into any extruded shape.

Generally, in order to dye the fibers or fiber products, the anionic dyes such as acid dyes, pre-metallised acid dyes, direct dyes or acid mordant dyes are dissolved in an exhaust dyeing bath, a continuous dyeing liquor, or a printing paste, which is adjusted to a suitable acidic condition by inorganic or organic acids such as acetic, oxalic, formic, citric, benzoic acid etc. The fibers or fiber products are then brought into contact with the dye solotion and heat treated at about 100 °C.

This heat treatment, especially when fiber products are dyed or printed, is very critical point in the process and should be made efficiently and with a high speed.

The auxiliaries according to this invention make the high speed possible. The fixation time without the auxiliaries in the printing process is about 3 to 15 minutes, depending on depth of the shade. Light shades fix at 3 minutes, dark shades need 15 minutes for full dyestuff fixation. But according to this invention, the fixation time can be shortened to about 1.5 to 5 minutes depending on the depth of the shade.

The invention is next descibed in more detail in the following examples.

Example 1 and Comparative Example 1

Polypropylene, melt index 18, (produced by Borealis N.V.) and 7 % by weight a copolymer of ethylene and dimethylaminopropyl methacrylamide (EDMAPMA) were melt blended and spun into filaments (1250/65 dtex) and tufted into a carpet.

The carpets have been printed with a mixture of Colour Index (C.I.) Acid Yellow 216:1, C.I. Acid Red 266 and C.I. Acid Blue 40 to have a dark brown trichromatic colour. The printing paste contains a thickener such as a Guar Gum, the dyestuffs and citric acid to ensure the protonation of the acid dyesites in the modified polypropylene. The citric acid is added until pH value of 3.0-3.5 is obtained.

Printing paste 1 contains the above mentioned elements (comparative)

Printing paste 2 contains on top of above mentioned components 20 g/kg of fixation speed improvement auxiliary (I), where

- R is a natural fatty alcohol radical based on coconut oil with 12-14 carbon atoms
- n = 2
- m = 2.5

Before printing the carpets are pre-wetted by means of a padding treatment, Pick-up (P.U.) 70 % with water containing citric acid for a pH = 3.0.

After printing, in order to fix the applied amount of dyestuff, the carpets go into a steamer for 2 minutes. Steaming conditions are 100 °C and relative humidity 50 %. After the fixation in the steamer, the carpets are rinsed in cold water and the colour depth of the fixed dyestuffs is evaluated visually or by means of spectrophotometer.

The carpet printed with the paste 2 has the double colour depth of the carpet printed with paste 1.

Example 2 and Comparative Example 2

The same polypropylene composition as in example 1 was melt spun into fibers which were used to make hanks, which have been exhaust dyed with C.I Acid Red 266 to obtain a deep red colour.

An exhaust dyebath is prepared with a solution of 2 % on weight of fabric (owf) of C.I. Acid Red 266 containing phormic acid to protonate the acid dyesites in the modified polypropylene. The pH is adjusted to 3.0-3.5.

Exhaust bath 1: containing only above mentioned components

Exhaust bath 2: containing above mentioned com-

ponents and 2 % of auxiliary (I), where

- R is same as in example 1
- n is 2
- m is 10

The hanks were put into the exhaust dyebath and heated up until 100 °C and stayed there until dyestuff exhaustion is obtained.

With exhaust dyebath 2, dyestuff migration from dyebath towards fibers started at 30 °C lower temperature than with exhaust dyebath 1.

The dyeing time for full exhaustion with dyebath 2 is 20 minutes and the dyeing time for exhaust dyebath 1 is 45 minutes.

Example 3 and Comparative Example 3

Same dyeable polypropylene composition as in Example 1 was melt spun into multifilaments and tufted into a loop pile carpet.

The same trichromatic composition of dyes as in example 1 was used to prepare a continuous dyeing bath to obtain a deep brown colour. The pH of this continuous dyeing liquor was adjusted to 3.0-3.5 with citric acid.

Continuous dyebath 1: contains the above mentioned components
Continuous dyebath 2: contains same as 1 and 10 g/litre of auxiliary (I), where

- R is same as in example 1
- n is 2
- m is 2.5

The carpets were continuos dyed by liquor application of the baths at P.U. of 250 %. After application, the colours were fixed by means of a steaming treatment (100 °C, 50 % relative humidity). The colour depth of the carpet dyed with bath 2 is double the colour depth of the carpet dyed with bath 1.

Claims

1. An improved method for dyeing or printing of polyolefins or fibers or fiber products made from polyolefins, **caracterized in that** the dye bath comprises a dyeing auxiliary which is of the general formula (I)

$$R - O - ((CH_2)_n - O)_m - CH_2 - COOH \qquad (I)$$

where

- R is a fatty alcohol radical having from 8 to 24 carbon atoms or an alkylphenol radical where the alkyl part contains from 8 to 9 carbon atoms
- n is 2 or 3
- m is from 0 to 150.

2. An improved method for dyeing or printing of polyolefin which have been modified by melt blending 100 parts per weight of polyolefin with 1-20 parts per weight of copolymer of ethylene and dialkylaminoalkyl methacrylamide or methacrylate and with 0-3 part per weight of alkali metal salt of organic carboxylic acid, for dyeing printing or fibers or fiber products made from the modified polyolefin, **characterized in that** to the dye bath comprises a dyeing auxiliary which is of the general formula (I)

$$R - O - ((CH_2)_n - 0)_m - CH_2 - COOH \qquad (I)$$

where

- R is a fatty alcohol radical having from 8 to 24 carbon atoms or an alkylphenol radical where the alkyl part contains from 8 to 9 carbon atoms
- n is 2 or 3
- m is from 0 to 150.

3. A method according to claim 1 or 2 **characterized in that** auxiliary agent is preferably

$$R - O - ((CH_2)_n - O)_m - CH_2 - COOH \qquad (I)$$

where

- R is a natural fatty alcohol radical based on coconut oil with 12 to 14 carbon atoms
- n is 2 or 3
- m is from 2.5 to 10

4. A method according to any of the claims 1 to 3 **characterized in that** the amount of the auxiliary agent (I) depending on the depth of shade and the dyeing method -2-50 g/kg for printing paste

- 0.1-5 % on weight of fabric (owf) for exhaust dyeing or
- 1-50 g/litre for continuous dyeing

5. A method according to any of claims 1 to 4 **characterized in that** the dye fixation time is reduced extensively depending on the dyeing method and the depth of shade.

6. Carpets and other products which are printed, exhaust dyed or continuous dyed acording to a method described in any of the preceding claims.

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EUROPEAN SEARCH REPORT

Application Number
EP 95 20 3603

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
X	US-A-3 926 553 (FUEST RONALD W) 16 December 1975 * column 3, line 40 - line 42 * * column 5, line 58 - column 6, line 24 * * column 6, line 55 - column 7, line 15; claims *	1-6	D06P3/79 D06P1/651 D06P1/613 D06P1/653
A	US-A-3 385 652 (WALTER ANDREW T ET AL) * the whole document *	1-6	
D,A	EP-A-0 039 207 (SUMITOMO CHEMICAL CO) 4 November 1981 * the whole document *	1-6	
D,A	EP-A-0 269 293 (SUMITOMO CHEMICAL CO) 1 June 1988 * the whole document *	1-6	

TECHNICAL FIELDS SEARCHED (Int.Cl.6)

D06P

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	24 May 1996	Blas, V

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
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T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
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